

An Improved Tensimeter-Still

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IN STUDIES of high-boiling derivatives of lactic acid, need arose for a device which would serve as a simple low-pressure still and also make possible accurate vapor pressure—i.e., boiling point—measurements in the low-pressure region—viz., 0.02 to 10 mm. of mercury.

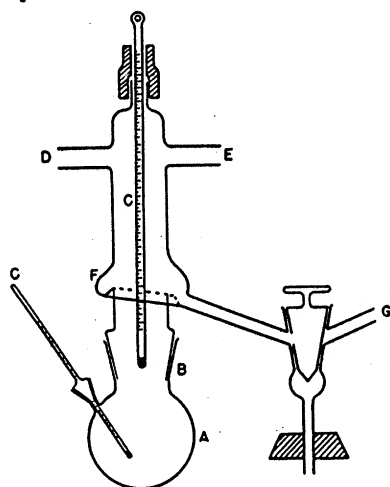


Figure 1. Tensimeter-Still

- A. Boiler, 500- or 1000-ml. flask with thermometer side arm
- B. 45/50 ground-glass joint
- C. Thermometers
- D. 12-mm. connection to vacuum gage
- E. 12-mm. connection to trap and pump
- F. Alembic, formed from 40-mm. tubing
- G. Connection to pump

Several types of stills were tried before the design described in this paper was evolved. The improved still has been in use for more than 2 years and has proved reliable and simple to operate over the desired range. It has been used to obtain vapor pressure information on a wide variety of lactic acid derivatives (10).

Various means have been used to overcome difficulties in obtaining accurate boiling point measurements at low pressures. The "automanometer still" of Hickman and Weyerts (8) exposes the distilland to a relatively high pressure drop between still pot and condenser, for it is precisely by measuring the pressure drop across one or more orifices that this still gains its usefulness. It is operable down to a condenser pressure of perhaps 0.5 mm. of mercury.

On the other hand, the tensimeter-hypsometer of Hickman, Jucker, and Embree (7) offers negligible pressure drop but operates on total reflux, so that distillation is impossible. This device, moreover, in the present authors' hands failed to operate satisfactorily above 2 mm., because of excessive bumping. It is stated to be operable down to 0.03 mm. of mercury.

At pressures below 0.01 to 0.03 mm., noncondensable gases diffuse against the distillate vapor stream and vitiate boiling point measurements (7). Hence it is futile to attempt such measurements at extremely low pressures, even though some substances can be distilled at such pressures in the tensimeter-still. If at approximately 0.03 mm. the boiling point of the distilland is too high to permit distillation without decomposition, it is advisable to use a molecular still, where permanent gases are pumped away efficiently and distillate molecules have a short path to the condenser.

The tensimeter-still is similar in appearance to commercial equipment that has been described recently (2); the latter, however, is recommended for use in the range 0.001 to 0.1 mm., and is stated to have a separation efficiency of less than one theoretical plate.

The present still gains its usefulness from vigorous agitation of the distilland, obtained by rocking the entire still to and fro. The agitation minimizes or eliminates superheating and inhomogeneities in the distilland, and thus facilitates accurate boiling point measurements and equilibrium distillation. The separation efficiency is at least one theoretical plate.

APPARATUS AND METHOD

The tensimeter-still (Figure 1) consists of a 500- or 1000-ml. round-bottomed short-necked flask fitted with a thermometer side arm and a 45/50 ground-glass joint. The joint is attached to a wide upright condenser with an alembic take-off located so that the vapor path is as short as possible. The condenser bears a thermometer and connections for a vacuum gage and pump. To maintain vapor-liquid equilibrium and avoid bumping, the still is suspended from the side tubes near the top of the condenser and rocked to and fro by a crank powered by a stirrer motor. The crank is attached at the ground joint after the flask is connected and the joint is well wrapped with asbestos tape. The joint is lubricated with silicone-type grease to eliminate the sticking sometimes encountered with ordinary grease.

In operation as a tensimeter, the rocker is started, and heat is applied with a mantle heater, while vacuum is maintained. When boiling begins, the connection to the pump is throttled down, and the pressure is adjusted to the desired value by means of a slow leak. Heating is continued until the sample is distilling gently. The heat input must be adjusted so that the difference between liquid and vapor temperatures is a minimum, indicating minimum superheating and pressure drop between flask and condenser. At several millimeters this difference is usually 1° C. or less, but at low pressures may become several degrees. To assist in condensing the vapors, a strip of moist cloth is sometimes wrapped around the condenser. The stopcock makes it possible to operate on total reflux (usually necessary on small samples).

The boiling point is taken as the vapor temperature at the prevailing pressure. To make certain that the system is in equilibrium, the boiling is continued until the vapor temperature remains constant. The pressure is then adjusted to another value, and the process repeated. It is possible to cover the range 0.03 to 10 mm. in a few hours. The data thus obtained are adequate for the preparation of the usual $\log P$ vs. $1/T$ charts.

For the pressure measurements, a triple-range McLeod gage covering the ranges 0 to 0.2, 0 to 1.0, and 0 to 20 mm. of mercury is used. This gage is useful because of its high precision at lower pressures, where the boiling point changes rapidly with pressure—for example, a pressure change of 0.1 mm. of mercury at 4 mm. changes the boiling point of butyl phthalate about 1° C. At 0.04 mm. a pressure change of only 0.003 mm. changes the boiling point 1° C. Hence if the boiling points are to be correct to 1° C., the pressure gage must have high precision at low pressures; this high precision is obtained with the triple-range gage. To keep condensable vapors out of the gage a trap cooled with solid carbon dioxide is used.

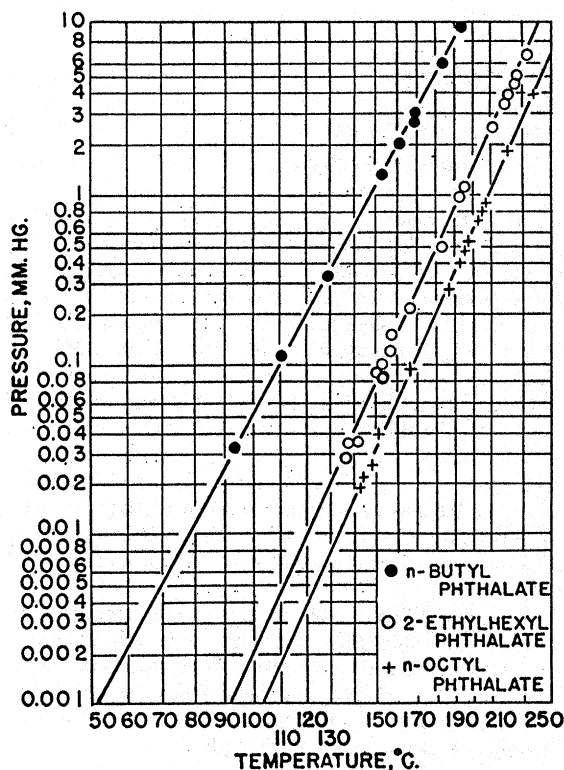


Figure 2. Vapor Pressure of Phthalates

The McLeod gage measures only the pressure of the permanent gases present. If the distilland has been well stripped of solvents and other light fractions, and if it is not undergoing decomposition during distillation, the McLeod measurements are reliable.

RESULTS AND DISCUSSION

The charts give boiling point curves for three common plasticizers (Figure 2) and for two potential plasticizers made from lactic acid (Figure 3), plotted as $\log P$ vs. $1/T$, °K. Each curve is linear, and although the experimental points go down only to 0.02 to 0.03 mm. of mercury, the curves have been extrapolated to 0.001 mm. The information in the literature (1, 3, 5, 7, 11) on the vapor pressures of these common plasticizers is compared with these data in Table I. The observed values were taken from the boiling point curves, and the literature values from similar published curves. The experimental points define a straight line that is in good agreement with published values; the observed boiling points of 2-ethylhexyl phthalate may be somewhat low, as this was a commercial plasticizer sample. As a measure of the agreement to be expected, it may be pointed out that six publications in the period 1930 to 1946 give the boiling point of butyl phthalate at 3 mm. as 166° to 170° C. (1, 3-5, 7, 11).

Extrapolation of the lines in Figure 2 gives 52° and 92° C. at 0.001 mm. for butyl and 2-ethylhexyl phthalates, respectively. The literature (direct determination, 7, 9) gives 56° and 96° C.

It is thus evident that the tensimeter-still can provide reliable vapor-pressure data over the range 0.03 to 10 mm. of mercury and

that a linear extrapolation of considerable usefulness may also be made to 0.001 mm.

Several factors tend to introduce errors into low-pressure measurements of boiling points, especially when the distilland is not adequately agitated: Evolution of vapor begins before the distilland reaches the boiling point, resulting in too low vapor temperature (6); the distilland becomes superheated because of poor heat transfer, resulting in too high vapor temperature; and in the distillation of a multicomponent distilland the surface layer becomes leaner in the more volatile components, resulting in non-equilibrium distillation, superheated vapor, and poor fractionation. The first two factors are important in tensimeter measurements because they tend to cause erroneous vapor-temperature observations. Fortunately, they have opposite effects and their net effect is thus reduced. In the low-pressure distillation of a mixture, all three factors must be considered, though it is believed that the first is of minor importance. The effects of the second and third factors, however, are additive and may be large, thus causing serious errors in observed boiling points. Their effect is minimized or virtually eliminated, however, by vigorous agitation of the distilland throughout the distillation. This is conveniently accomplished in the tensimeter-still by the reciprocating motion of the still imparted by the motor-activated crank. It is believed that the satisfactory results obtained in the present work were possible with equipment of this general type only because efficient agitation of the distilland was achieved.

The agreement of these tensimeter data with vapor-pressure information obtained by other means [pendulum tensimeter (7), direct weighing and molecular dew (9)] indicates that a recent suggestion that "low pressure tensimeters relying on residual gas to measure the vapor pressure must be highly inaccurate in this range (0.15 mm.)" (8) is hardly valid. This suggestion was made on the basis of an observation during a distillation under conditions much different from those in the tensimeter-still.

As a still, the device is useful in the preparation of many high-boiling compounds, provided a low fractionating efficiency is sufficient—that is, the boiling points of the fractions to be separated are fairly wide apart. The preparation of dicarboxylic acid esters of various lactates (10) may be used to illustrate the use of the tensimeter-still in distilling organic compounds. After the crude

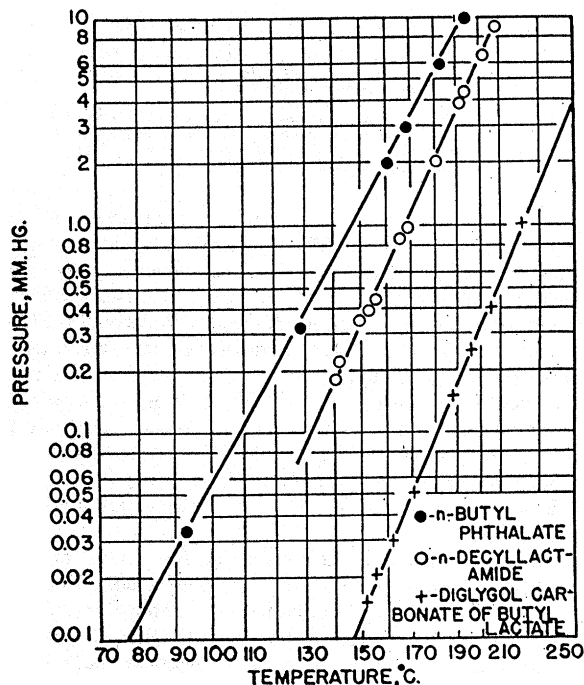


Figure 3. Vapor Pressures of Lactic Acid Derivatives

Table I. Comparison of Boiling Points with Published Values

Plasticizer	Boiling Points at Various Pressures					
	4 mm. of Hg		0.4 mm. of Hg		0.04 mm. of Hg	
	Obsd.	Lit.	Obsd.	Lit.	Obsd.	Lit.
Butyl phthalate	174	172	132	133	96	97
2-Ethylhexyl phthalate	220	225	177	179	141	141
n-Octyl phthalate	237	238	191	192	153	...

reaction mixture has been obtained, the lower boiling reagents are distilled from the product in a Vigreux still, and then the residue is distilled at low pressure in the tensimeter-still. The product thus obtained may be redistilled to obtain vapor-pressure data; if the reaction is clean-cut, however, the distillation and vapor-pressure determinations may be effected simultaneously. The reliability of the boiling point measurements indicates that the tensimeter-still has a separating efficiency of at least one theoretical plate.

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